

# DRIFT ANALYSIS OF SURFACE OXYGEN COMPLEXES ON SOOT FORMED BY METAL OXIDES

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Keywords : DRIFT, Surface Oxygen Complexes, Metal Oxides.

## INTRODUCTION

At the Delft University of Technology a project concerning the catalytic removal of soot from diesel exhaust gases is being carried out. We are interested in a catalyst for the oxidation of soot particulates because: (i) diesel engines can no longer meet the requirements of the particulate (soot) emission standards, and (ii) collection of soot in a monolithic filter and simultaneous oxidation at diesel exhaust gas temperatures (600 K) is considered to be the best option to abate the emission of soot.

The mechanism of catalytic oxidation reactions of carbonaceous materials has been the subject of many researchers over the last decades. Although it has been generally expected that Surface Oxygen Complexes (S.O.C.) play an essential role in these reactions, their chemical nature, and interaction with catalysts and the oxidant ( $\text{CO}_2$ ,  $\text{H}_2\text{O}$  or  $\text{O}_2$ ) have hardly been reported. A powerful tool in analyzing carbonaceous materials is Fourier Transformed Infrared spectroscopy and in particular Diffuse Reflectance Infrared Fourier Transformed (DRIFT) spectroscopy. Several research groups have analyzed coal of several ranks using this technique *e.g.* (1-3). Also *in situ* studies regarding the oxidation of coal have been performed (4-6), as well as DRIFT studies on oxidized soot (7,8) and PF chars (9). Very few researchers have used DRIFT spectroscopy to analyze the catalytic oxidation of carbon or soot. Cerfontain has studied the alkali carbonate catalyzed carbon oxidation by  $\text{CO}_2$  by means of FT-IR (10), but carbon oxidation involving  $\text{O}_2$  and (transition) metal oxides have only been reported by us (11). It has been shown that during burn-off certain metal oxides enhance the amount of S.O.C. on the soot surface, while others do not. This observation has been explained by two different reaction mechanisms: (i) a redox mechanism and (ii) a spill-over mechanism (11). However, these results were obtained with catalyst/soot mixtures with a high catalyst to soot ratio (1:1, *i.e.* 50 wt%). In this paper DRIFT analyses of partially converted soot by impregnated Fe-, Co-, Cr-, K-, and Ca- oxides (10 wt%) are presented, which validates a comparison of these analyses with literature data on catalyzed carbon and coal gasification.

## EXPERIMENTAL

Printex-U (a model soot, purchased from Degussa) was used to perform the oxidation studies. This soot has a BET surface area of  $96.0 \text{ m}^2 \text{ g}^{-1}$  and contains approximately 5 wt% of adsorbed hydrocarbons and only 0.2-0.4 wt% sulfur (12).

Analytical grades of the (transition) metal nitrates were used to impregnate the soot. An amount of the nitrate, corresponding with 10 wt% of the most stable oxide ( $\text{Fe}_2\text{O}_3$ ,  $\text{Co}_3\text{O}_4$ ,  $\text{Cr}_2\text{O}_3$ ,  $\text{K}_2\text{O}$ , and  $\text{CaO}$ ) was dissolved in 200 ml ethanol, followed by addition of 200 mg soot to the solution. The ethanol was removed at 325 K under reduced pressure in a rotating evaporator. The black powder could be recovered by scratching it from the glass wall of the flask with a spatula.

Partial conversion of the soot was accomplished in a so-called six-flow reactor. A six-flow experiment was carried out by packing five quartz reactors (one reactor was used as a blank) with approximately 25 mg of the impregnated soot/metal nitrate mixture, sandwiched between two layers of SiC. A controlled flow of 150 ml/min. 10 vol%  $\text{O}_2$  in Ar was led through the reactors. A non dispersive infrared detector (Hartmann & Braun Uras 10 E) was used to measure  $\text{CO}$ ,  $\text{CO}_2$  and  $\text{NO}$  concentrations. These concentrations were measured alternately every 90 seconds in each reactor. A multiposition valve (Valco) selected the reactor for analysis. The partial conversions were obtained isothermally @ 575 K (K, Co) and @ 585 K (Ca, Fe, Cr). The final temperature was reached with a ramp of 5 K/min. The amount of soot converted was determined by integrating the  $\text{CO}$  and  $\text{CO}_2$  concentrations with time. After reaction SiC was separated from the soot sample before analysis.

DRIFT spectra were recorded on a Nicolet Magna 550 spectrometer equipped with a DTGS detector and a Spectratech DRIFT accessory. KBr was used as a diluent. Spectra are displayed in  $8 \text{ cm}^{-1}$  resolution in absorbance reflectance mode against a (*non*-converted) soot in KBr background.

## RESULTS & DISCUSSION

### Transition metal nitrates

A typical result of the analysis of one reactor in a sixflow measurement is shown in figure 1. The variations in the CO, CO<sub>2</sub> and NO concentrations as a function of time are given for the Fe(NO<sub>3</sub>)<sub>3</sub>/soot sample. Decomposition of Fe(NO<sub>3</sub>)<sub>3</sub> into N<sub>2</sub>O, NO and NO<sub>2</sub> (the concentrations of N<sub>2</sub>O and NO<sub>2</sub> were not determined) occurs at approximately 450 K. As NO<sub>2</sub> is a strong oxidant, reaction of NO<sub>2</sub> with soot results in NO, CO and CO<sub>2</sub> formation (13). The reaction of NO<sub>2</sub> with soot is reflected by high NO, CO and CO<sub>2</sub> concentrations in the first 6 ks of the reaction, when the temperature is still increasing with time. After the temperature has become constant @ 585 K (the temperature was isotherm between the verticle dashed lines), the CO and CO<sub>2</sub> concentrations decrease exponentially with time. A similar trend was obtained for the Co(NO<sub>3</sub>)<sub>2</sub>/soot sample @ 575 K (not shown). By integration of the CO and CO<sub>2</sub> concentrations, soot conversion was calculated to be 20% for the Fe(NO<sub>3</sub>)<sub>3</sub>/soot, and 50% for the Co(NO<sub>3</sub>)<sub>2</sub>/soot mixture respectively.

Variations in the CO, CO<sub>2</sub> and NO concentrations @ 585 K for the impregnated Cr(NO<sub>3</sub>)<sub>3</sub>/soot mixture are shown in figure 2. Similar to the Fe(NO<sub>3</sub>)<sub>3</sub> measurement, a rapid decomposition of the nitrate into (presumably) Cr<sub>2</sub>O<sub>3</sub> can be observed at 400 K, accompanied by high NO, CO and CO<sub>2</sub> concentrations. In the isothermal part, the development of the CO and CO<sub>2</sub> concentrations is quite different from the Fe(NO<sub>3</sub>)<sub>3</sub> sample. Instead of a decay, a slow increase in the CO and CO<sub>2</sub> concentrations can be observed. A similar result has been obtained for a mechanical mixture of Cr<sub>2</sub>O<sub>3</sub> and soot (14). The soot conversion was calculated to be 50%. Another six-flow experiment was performed upto a conversion level of 20%.

The DRIFT spectra of the partially converted Fe(NO<sub>3</sub>)<sub>3</sub>/soot (20% (A)), Co(NO<sub>3</sub>)<sub>2</sub>/soot (50% (B)) and Cr(NO<sub>3</sub>)<sub>3</sub>/soot (20% (C) and 50% (D)) samples are shown in figure 3. Infrared absorptions which are typical for compounds containing (hydrated) nitrate groups (1560-1540, 1020-1070, 800 and 760 cm<sup>-1</sup>) (15) are not present in the spectra. The absorptions located @ 665 and 578 cm<sup>-1</sup> (spectrum B) can be ascribed to the spinel vibrations of Co<sub>3</sub>O<sub>4</sub>. The broad absorption band @ 549 cm<sup>-1</sup> is ascribed to Cr<sub>2</sub>O<sub>3</sub> (spectra C and D). Hence, confirming the six-flow analysis, the transition metal nitrates were completely converted into their oxides. Generally three types of Surface Oxygen Complexes (S.O.C.) can be identified with DRIFT on soot (or carbon) surfaces: (i) ethers (1250-1275 cm<sup>-1</sup>), (ii) quinones (1600-1620 cm<sup>-1</sup>), and (iii) lactones (1730-1740 cm<sup>-1</sup>) (9). On the surface of the partially converted soot by Cr(NO<sub>3</sub>)<sub>3</sub> (Cr<sub>2</sub>O<sub>3</sub>) large quantities of these S.O.C. were formed. The spectra of the Fe<sub>2</sub>O<sub>3</sub> and Co<sub>3</sub>O<sub>4</sub> samples show approximately the same amount of S.O.C. as were formed *non-catalytically* on soot under similar conditions. These results are in agreement with the results obtained for mechanical mixtures of Cr<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub> and Co<sub>3</sub>O<sub>4</sub> with soot (11).

### Potassium nitrate

The activity in the soot oxidation of KNO<sub>3</sub> is shown in figure 4. KNO<sub>3</sub> decomposition is not as fast as the decomposition of the transition metal nitrates. Moreover, the maxima in the CO and CO<sub>2</sub> concentrations do not coincide with the maximum in the NO concentration. Apparently the peculiar "peaks" in the CO and CO<sub>2</sub> concentrations are not entirely explained by the NO<sub>2</sub>/soot reaction. After the "peaks", the CO and CO<sub>2</sub> concentrations decay linearly in time. The calculated conversion was 75%.

DRIFT spectra of KNO<sub>3</sub>/soot samples at conversion levels of 0% (A), 50% (B), 75% (C), and >90% (D) are shown in figure 5. Spectrum A corresponds quite well with the spectrum of pure KNO<sub>3</sub> (the 1383 cm<sup>-1</sup> vibration can be assigned to a nitrate vibration (15)). After 50% soot conversion, the 1383 cm<sup>-1</sup> vibration is no longer present. Hence, the nitrate has decomposed. Although ether-like species are not so clearly present (@ 1250-1300 cm<sup>-1</sup>), the absorptions located @ 1721 cm<sup>-1</sup> and 1595 cm<sup>-1</sup> indicate that (a) potassium oxide catalyzes the formation of S.O.C. These absorptions are increasing with the conversion level, and shifted to somewhat lower wavenumbers, compared to the spectra shown in figure 3. This might indicate that a potassium oxide is in the vicinity of the S.O.C.

Carbonate formation is witnessed by broad absorption bands @ 1456 cm<sup>-1</sup> and 871 cm<sup>-1</sup> (15,22), which are clearly present in the spectrum of the sample converted to >90% (spectrum D). Other absorption bands, @ 1118 cm<sup>-1</sup> and 620 cm<sup>-1</sup>, are increasing with conversion. Also impregnated Rb and Cs oxides cause the formation of these absorptions during burn off. We are still speculating on the nature of the (potassium) compound responsible for these absorptions. The assignment of these bands to potassium sulfate, which has vibrations in the 1100-1200 cm<sup>-1</sup> region, is not likely, because the amount of sulfur initially present in the soot (Printex-U) is low and the sulfate-ion has a more complex IR pattern than shown in figure 5 (15). The 1118 cm<sup>-1</sup> band has been observed by other authors in the K<sub>2</sub>CO<sub>3</sub> catalyzed carbon gasification with CO<sub>2</sub> (10) and steam (16). Cerfontain (10) and Freriks (16) did not detect the 620 cm<sup>-1</sup> band, because they did not record their spectra below 1000 cm<sup>-1</sup>. In our opinion this absorption is related to the 1118 cm<sup>-1</sup> one. The 1118 cm<sup>-1</sup> band has been assigned to a potassium phenolate (10). However,

the carbon-oxygen vibration of potassium phenolate (or phenoxide) occurs at much higher wavenumbers (around  $1300\text{ cm}^{-1}$  (17), verified by ourselves). The mass difference of a phenoxide and a poly-aromatoxide ion can only partly account for a red shift of  $150\text{ cm}^{-1}$ . Unless the frequency of C-OK vibrations is strongly influenced by the vicinity of other C-OK groups (e.g. in the compound proposed by Freriks (16)) or other oxygenated species, the assignment of the  $1118\text{ cm}^{-1}$  vibration to phenolate species is not very likely. A second proposition for the assignment of the  $1118\text{ cm}^{-1}$  band is based on the following: the structure of alkali metal catalysts under gasification conditions is thought to be a potassium oxide ( $\text{K}_2\text{O}$ ) cluster attached to the carbon surface (18). It has been shown that  $\text{CO}_2$  adsorption on the potassium oxide cluster is very strong (18,19). Therefore, the  $1118$  and  $620\text{ cm}^{-1}$  absorptions might be the result of  $\text{CO}_2$  (formed during soot oxidation) strongly interacting with a potassium oxide cluster. Interestingly, similar absorptions have been reported in studies on  $\text{CO}_2$  adsorption on  $\text{Cu}_2\text{O}$  (20) and  $\text{CuO}$  (21).

#### **Calcium nitrate**

Decomposition of calcium nitrate is less rapid than decomposition of the transition metal nitrates (figure 6). Although some NO (and CO and  $\text{CO}_2$ ) production takes place during the temperature ramp, a considerable amount of nitrate decomposes in the isothermal stage. For some reason, the decomposition rate increases with time. The NO, CO and  $\text{CO}_2$  concentrations run parallel, indicating that the primary product of nitrate decomposition is  $\text{NO}_2$ , which subsequently oxidizes the soot, resulting in the observed products. After complete decomposition of  $\text{Ca}(\text{NO}_3)_2$ , a second increase in reaction rate can be observed. The measurement shown in figure 6 resulted in 50% soot conversion.

DRIFT spectra of  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ /soot samples (0% (A), 20% (B), 50% (C) and >90% (D) soot conversion) are shown in figure 7. After preparation several absorptions occur in the  $500\text{--}2000\text{ cm}^{-1}$  region of the spectrum, due to nitrate vibrations (@  $1384$ ,  $1046$  and  $838\text{ cm}^{-1}$ ). The absorption band @  $1635\text{ cm}^{-1}$  can be ascribed to the O-H bending mode of water of crystallization in  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  (23). The broad band located @  $1433\text{ cm}^{-1}$  is also present in the DRIFT spectrum of pure  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ . After 20% soot conversion @  $575\text{ K}$ , the nitrate vibrations are still present, which is in agreement with six-flow data. The  $1433\text{ cm}^{-1}$  band has broadened and a new vibration, located at approximately  $1579\text{ cm}^{-1}$ , can be observed. At higher conversions (spectra C and D) the vibrations due to the nitrate group have disappeared and are replaced by the vibrations ascribed to the carbonato group ( $\text{CaCO}_3$  (14,23,24)) @  $712\text{ cm}^{-1}$ ,  $875\text{ cm}^{-1}$ , centred @  $1436\text{ cm}^{-1}$ , and  $1795\text{ cm}^{-1}$ . The  $1579\text{ cm}^{-1}$  band has shifted somewhat to  $1587\text{ cm}^{-1}$ . Also a broad absorption band starts to develop @  $1142\text{ cm}^{-1}$ . This band is clearly visible in the spectrum of the >90% soot conversion. In the latter spectrum, the  $1587\text{ cm}^{-1}$  vibration is no longer present.

Absorptions due to regular lactone, quinone and ether like complexes are hardly visible. However, the  $1587\text{ cm}^{-1}$  absorption is related to the presence of soot, because this absorption frequency is not visible after 90% soot conversion. Probably this band is due to quinone species. The shift of approximately  $20\text{ cm}^{-1}$  might be caused by some kind of interaction with a Ca-ion. The broad  $1142\text{ cm}^{-1}$  absorption might be related to the  $1118\text{ cm}^{-1}$  absorption band observed in the  $\text{KNO}_3$ /soot spectra.

#### **Mechanistic considerations**

The investigated metal nitrate precursors show an increasing reactivity in the order  $\text{K} > \text{Co} > \text{Cr} > \text{Fe} = \text{Ca}$ . The activities of the impregnated samples are higher than the activities found for the mechanical mixtures of the metal oxides and soot (11). Especially the activity of the impregnated chromium nitrate is much higher than the activity of bulk  $\text{Cr}_2\text{O}_3$ . The differences in reactivity might be explained by a better dispersion of the oxides formed after decomposition of the impregnated nitrates. X-Ray Diffraction and Transmission Electron Microscopy studies are currently being performed to determine the particle size of the various impregnated nitrates and oxides.

The DRIFT spectra shown in this paper indicate that the formation of S.O.C. is dependent on the catalyst used. In the presence of K, Ca and Cr catalysts, S.O.C. are catalytically formed. The differences in CO and  $\text{CO}_2$  concentration profiles shown in figures 1,2,4 and 6, are very likely related to this formation of S.O.C. Catalysts which do not enhance the formation of S.O.C., show an exponential decay, while catalysts which increase the amount of S.O.C. show a less pronounced activity loss (K), or even an activity increase (Cr, Ca). The differences in reactivity profiles is discussed in more detail elsewhere (14).

A redox cycle is often proposed as the most likely mechanism by which metal oxides operate in the oxidation of carbon (e.g. (25,26)). Other authors mention spill-over of oxygen to explain catalytic carbon oxidation. Baker et al. (27) argued, explaining their Controlled Atmosphere Electron Microscopy (CAEM) studies, that  $\text{Cr}_2\text{O}_3$  was able to dissociate molecular oxygen and to transfer the activated oxygen to the carbon surface. Eventually, reaction occurred

at the graphite edges. This might indicate that the enhanced formation of S.O.C. is related with oxygen spill-over.

Oxygen spill-over has never been proposed for alkali metal carbon gasification reactions (28-31). However, the mechanism proposed by Meijer and Moulijn (21) involves the transfer of oxygen from a K-oxide cluster to an active carbon site, which could be interpreted as spill-over. Reaction of this transferred oxygen results in the formation of S.O.C. Kapteijn *et al.* (32), discussing a transient isotopic CO<sub>2</sub> gasification study, describe several kinds of S.O.C., which they indicate as C(O)C<sub>2</sub>(O) (lactone) and C<sub>2</sub>(O) (semi-quinone). The DRIFT spectra presented in this paper show, in agreement with the literature data, that upon carbon (soot) oxidation several S.O.C. are formed, probably in the vicinity of a potassium oxide cluster.

The spill-over effect was also mentioned by Kyotani and Tomita *et al.* in relation with Ca catalyzed graphite oxidation (33-36). Although Martin and Kyotani *et al.*, using SIMS and TPD, did not reveal the nature of the S.O.C. formed after Ca catalyzed oxidation (35), they indicated that the distribution of the S.O.C. corresponded to the distribution of the Ca catalyst. This is in agreement with the fact that we observe a shift of the 1605 cm<sup>-1</sup> quinone band to lower wavenumbers, which could be induced by the presence of Ca ions. The fact that we were unable to detect lactone species (or C(O,O) (33)), formed by reaction of a C(O) complexes with an activated oxygen atom, might be due to a very fast, Ca induced, desorption of those complexes (as CO<sub>2</sub>). The nature and role of the species absorbing @1142 cm<sup>-1</sup>, is not clear at this moment.

Evaluating the presented DRIFT spectra and literature mentioned, we believe that the catalytic formation of S.O.C. must be related to some kind of oxygen spill-over mechanism. The intensity and frequency of the absorptions of the S.O.C. might be indicative for the stability and the vicinity of a metal oxide. Catalysts which do not enhance the amount of S.O.C. are thought to be active according to a redox-mechanism (11,14).

## CONCLUSIONS

- The transition metal nitrates decompose in air at approximately 450 K. DRIFT analysis revealed that metal oxides are formed upon decomposition.
- The results of the DRIFT analyses of impregnated samples are in agreement with the results presented earlier (11) for mechanically mixed soot/transition metal oxide mixtures. Cr<sub>2</sub>O<sub>3</sub> causes an enhancement of the amount of S.O.C. (compared to non-catalytic oxidation), whereas Co<sub>2</sub>O<sub>4</sub> and Fe<sub>2</sub>O<sub>3</sub> do not.
- Alkali metal nitrates are less easily converted into their corresponding oxides. After decomposition an alkalimetal oxide attached to the carbon surface is being formed. The exact nature of this compound remains to be elucidated.
- Alkali metal oxides enhance the amount of S.O.C. The IR absorption band of the quinone species is shifted from 1605 cm<sup>-1</sup> to 1585 cm<sup>-1</sup>. Also the lactone vibration (1735 cm<sup>-1</sup>) is shifted to lower wavenumbers, indicating the vicinity of a potassium ion.
- Ca(NO<sub>3</sub>)<sub>2</sub> is the most stable of the nitrates investigated, and decomposes into CaCO<sub>3</sub> upon soot oxidation. Also an "alkali metal like" complex on the soot surface is eventually being formed. CaCO<sub>3</sub> probably generates quinone species, whereas lactones are not formed.
- The catalytic formation of S.O.C. by Cr, K, and Ca, as shown by the DRIFT spectra presented in this paper, is tentatively explained by "spill-over" of activated oxygen. This is in reasonable agreement with data reported in the literature.

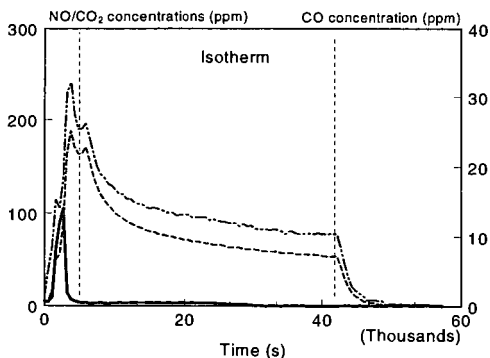
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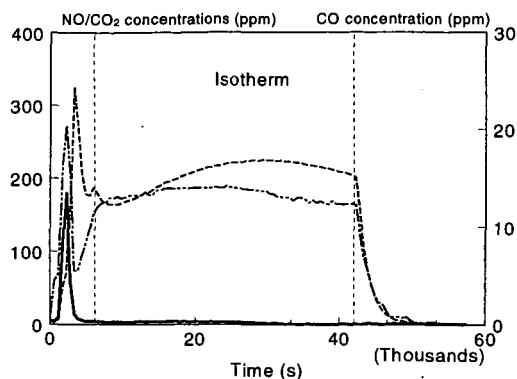
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#### ACKNOWLEDGEMENT

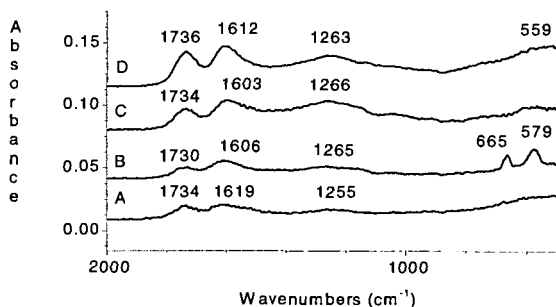
The research described in this publication was supported by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organisation for Scientific Research (NWO).



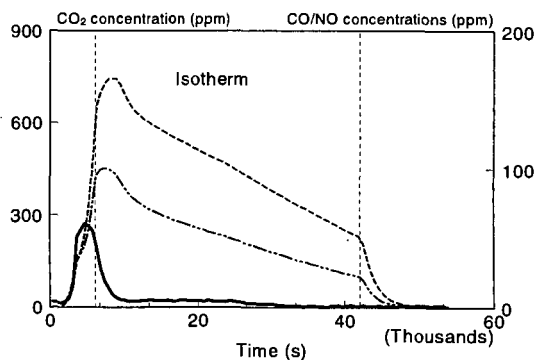
**Figure 1.**  $\text{Fe}(\text{NO}_3)_3$  catalyzed soot oxidation. Development of NO (solid),  $\text{CO}_2$  (dash) and CO (alternating dash) concentrations in time.



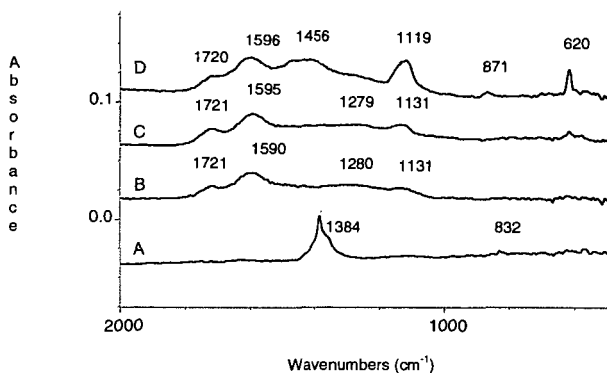
**Figure 2.**  $\text{Cr}(\text{NO}_3)_3$  catalyzed soot oxidation. Development of NO (solid),  $\text{CO}_2$  (dash) and CO (alternating dash) concentrations in time.



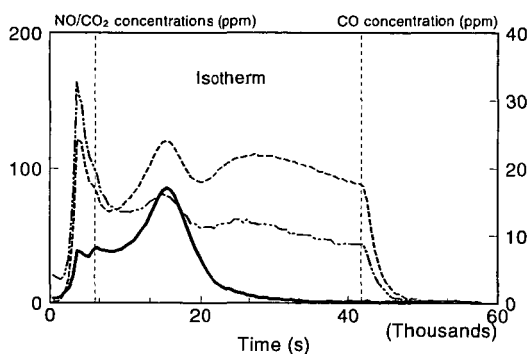
**Figure 3.** DRIFT spectra of partial converted soot by transition metal oxides: A.  $\text{Fe}_2\text{O}_3$ -20%, B.  $\text{Co}_3\text{O}_4$ -50%, C.  $\text{Cr}_2\text{O}_3$ -20%, D.  $\text{Cr}_2\text{O}_3$ -50%.



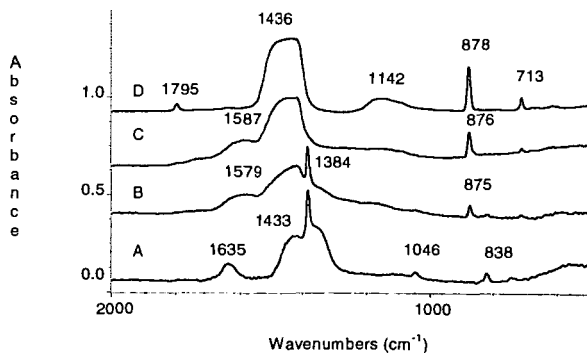
**Figure 4.**  $\text{KNO}_3$  catalyzed soot oxidation. Development of NO (solid),  $\text{CO}_2$  (dash) and CO (alternating dash) concentrations in time.



**Figure 5.** DRIFT spectra of partial converted  $\text{KNO}_3$  impregnated soot :  
A. 0%, B. 50%, C. 75%, D. >90%



**Figure 6.**  $\text{Ca}(\text{NO}_3)_3$  catalyzed soot oxidation. Development of NO (solid),  $\text{CO}_2$  (dash) and CO (alternating dash) concentrations in time.



**Figure 7.** DRIFT spectra of partial converted  $\text{Ca}(\text{NO}_3)_2$  impregnated soot :  
A. 0%, B. 20%, C. 50%, D. >90%